Reprinted from THE JOURNAL OF CHEMICAL PHYSICS, Vol. 51, No. 12, 5414–5419, 15 December 1969
Printed in U. S. A.

Calculation of Predissociation Rates of the $B\ ^3\Pi_{0^+u}$ State of I_2

ARA CHUTJIAN*
Department of Chemistry University of Southern California, Los Angeles, California
(Received 26 June 1969)

A comparison of the purely radiative decay rates of vibrational levels of the $B\ ^3\Pi_{0^+u}$ state of I_2 with total decay rates obtained from several independent lifetime measurements has indicated a significant amount of spontaneous predissociation of the B state. We present here a calculation of the observed relative predissociation rates by means of a model consisting of a repulsive 1_u state which is coupled to the $v'J'$ levels of the B state by rotational and electronic angular-momentum terms neglected in the zeroth-order Hamiltonian. The heterogeneous predissociation rate between a bound $v'J'$ level and a continuum level at the same energy is calculated from Kronig's theory using exact wavefunctions for both levels. The dependence of this rate on the rotational level J' is taken into account, together with the fractional population of the $v'J'$ levels which were excited in the measurement of the total decay rates. Excellent agreement is found between the calculated and observed relative predissociation rates at regions about v' of 14, 25, and 50 of the B state for one position of the repulsive state lying very near the repulsive wall of the B state over the energy range 17 300–20 000 cm^{-1}. The position of this state relative to the $B\ ^3\Pi_{0^+u}$ and $A\ ^3\Pi_{1u}$ states agrees well with Mulliken's prediction of the location of the $^1\Pi_{1u}$ state of I_2.

INTRODUCTION

Recent studies of the I_2 molecule have centered about several properties that can be related to the effects of repulsive electronic states which arise from the lowest $^2P_{3/2}+^2P_{3/2}$ iodine atom configuration. In the experiments of Wasserman, Falconer, and Yager,[1] Busch,

* Present address: Physics Section, Jet Propulsion Laboratory, Pasadena, California 91103.

[1] E. Wasserman, W. E. Falconer, and W. A. Yager, J. Chem. Phys. 49, 1971 (1968). This work is reported in more detail in Ber. Bunsenges. Physik. Chem. 72, 248 (1968).

Mahoney, Morse, and Wilson,[2] and Brewer and Tellinghuisen,[3] $^2P_{3/2}$ atoms have been seen as a result of excitation into the banded region of the B state. Other measurements of the magnetic-field quenching of the B–X fluorescence by Degenkolb, Steinfeld, Wasserman, and Klemperer,[4] and line-strength measurements by Chutjian and James[5] have shown the presence of a number of processes producing two $^2P_{3/2}$ iodine atoms, and have given quantitative measurements of their rates. Degenkolb *et al.* were also able to trace out a portion of the repulsive 0^-_u state responsible for the magnetically induced quenching.

In the present work we explore the predissociative property of the B state a bit further. By assuming a repulsive state of the form r^{-12} (correlating to ground-state iodine atoms), we were able to obtain very good agreement with the observed predissociation rates[5] of vibrational regions of the B state whose lifetimes had been measured with atomic-line excitations by two independent techniques.[6,7] The calculated relative rates were quite sensitive to the position of the repulsive state, and good agreement was found at one unique position of the state. This position agrees very closely with that predicted by Mulliken for the $^1\Pi_{1u}$ state, and it is this state which is causing the spontaneous predissociation of the B state.

THEORETICAL CONSIDERATIONS

Following the treatment of Wentzel[8] and Kronig,[9] we can write the nonradiative predissociation rate A_{nr} as

$$A_{nr}(\text{sec}^{-1}) = (2\pi/\hbar)\ |\ \langle \Omega_c E_c J\ |\ \mathbf{H}'\ |\ \Omega_b v J\rangle\ |^2, \quad (1)$$

where the subscripts b and c denote bound and continuum states, respectively. Here, $2\pi\hbar$ is Planck's constant, and the quantity in the brackets is the matrix element connecting the bound electronic, vibrational, rotational level, having quantum numbers Ω_b, v, and J, with the continuum state at the same energy E_c as the bound state, and having an electronic angular momentum Ω_c and a rotational barrier $J(J+1)/r^2$, where r is the internuclear separation. The operator $\mathbf{H}'$ is that part of the total Hamiltonian operator for the nuclei and electrons which was neglected in the zeroth-order approximations $\langle \Omega_c E_c J\ |$ and $|\ \Omega_b v J\rangle$. The detailed form of $\mathbf{H}'$ is given by Kronig for homogeneous ($\Omega_c - \Omega_b = \Delta\Omega = 0$) and heterogeneous ($\Delta\Omega = \pm 1$) predissociations. In the case of I_2 we may only have a heterogeneous predissociation ($1_u \leftarrow 0^+_u$, $\Delta\Omega = +1$) to either or both the nearby $A^3\Pi_{1u}$ and $^1\Pi_{1u}$ states, and $\mathbf{H}'$ in this case is the product of a rotational B value $(\hbar^2 N_0/2\mu)r^{-2}$, (here, μ is the reduced mass of I_2 in Astons and N_0 is Avogadro's number), and certain electronic and nuclear angular-momentum operators. The electronic operators are of the form

$$\sum_i [\xi_i(\partial/\partial\eta_i) - \eta_i(\partial/\partial\xi_i)],$$

where the sum is taken over the coordinates (referred to the molecular frame) of the i electrons of the system, and where two further sums arise by a cyclic variation in the coordinates $\xi\eta\zeta$. These terms give rise to the electronic coupling between 1_u and 0^+_u states, and the explicit form of the electronic contribution $R_e(r)$ to the predissociation will be these angular-momentum operators averaged over the zeroth-order electronic wavefunctions. The nuclear-rotation operator is of the form $\partial/\partial\theta$, where θ is the angle between the internuclear axis and a space-fixed z axis, which has nonzero matrix elements for $\Delta\Omega = \pm 1$ given by[9] $[(J \pm \Omega_b + 1)(J \mp \Omega_b)]^{1/2}$.

The total overlap between the two electronic states will then be the product of a vibrational overlap $\langle E_c J\ |\ r^{-2}\ |\ vJ\rangle$ (whose squared magnitude is analogous to the Franck–Condon factor in bound–bound dipole transitions), the nuclear-rotation matrix element given above, and the electronic overlap $R_e(r)$, whose value can depend on the position of the nuclei, but which we will assume to be a constant R_e in our treatment. Equation (1) then takes the form

$$A_{nr} = (2\pi/\hbar)(\hbar^3 N_0^2/8\pi\mu^2 c)(J \pm \Omega_b + 1)(J \mp \Omega_b) \times |\ R_e\ |^2\ |\ \langle E_c J\ |\ r^{-2}\ |\ vJ\rangle\ |^2, \quad (2)$$

where c is the speed of light and where the normalization of the last factor is per unit energy (cm^{-1}) range.

In a particular experimental measurement where several v, J levels may contribute to the predissociation, Eq. (2) must be summed over these levels, each weighted by the fraction f_{vJ} of the population in that level. Equation (2) then takes the final form for predissociation of a region of several v's and J's:

$$A_{nr} = (\hbar^2 N_0^2/4\mu^2 c)\ |\ R_e\ |^2 \sum_{v,J\ \text{region}} f_{vJ} J(J+1) \times |\ \langle E_c J\ |\ r^{-2}\ |\ vJ\rangle\ |^2, \quad (3)$$

where

$$\sum_{v,J\ \text{region}} f_{vJ} = 1,$$

and where we have set Ω_b to zero for the B state of I_2. Using the values $\hbar = 1.05450 \times 10^{-27}$ erg·sec, $N_0 = 6.02252 \times 10^{23}$ mole^{-1}, $c = 2.997925 \times 10^{10}$ cm/sec, and $\mu = 63.4522$ g/mole, we get that $\hbar^2 N_0^2/4\mu^2 c = 0.835363 \times 10^{11}$ $\text{sec}^{-1}\cdot\text{cm}^{-1}$ Å^4.

We obtain A_{nr} experimentally by taking the difference between the total and radiative rate of depopulation of several vibrational regions of the B state for which the total rate of depopulation was measured. These regions consist of rotational levels in $v = 14, 15, 16$ excited by the sodium D lines (λ5889, 5895 Å), levels in $v = 25, 26, 28$ excited by the mercury green line (λ 5461

[2] G. E. Busch, R. T. Mahoney, R. I. Morse, and K. R. Wilson, J. Chem. Phys. **51**, 837 (1969).
[3] L. Brewer and J. Tellinghuisen (unpublished results).
[4] E. O. Degenkolb, J. I. Steinfield, E. Wasserman, and W. Klemperer, J. Chem. Phys. **51**, 516 (1969).
[5] A. Chutjian and T. C. James, J. Chem. Phys. **51**, 1242 (1969).
[6] A. Chutjian, J. K. Link, and L. Brewer, J. Chem. Phys. **46**, 2666 (1967).
[7] S. P. Davis and D. E. Grimes (unpublished results).
[8] G. Wentzel, Z. Physik **43**, 524 (1927); Physik. Z. **29**, 321 (1928).
[9] R. Kronig, Z. Physik **50**, 347 (1928).

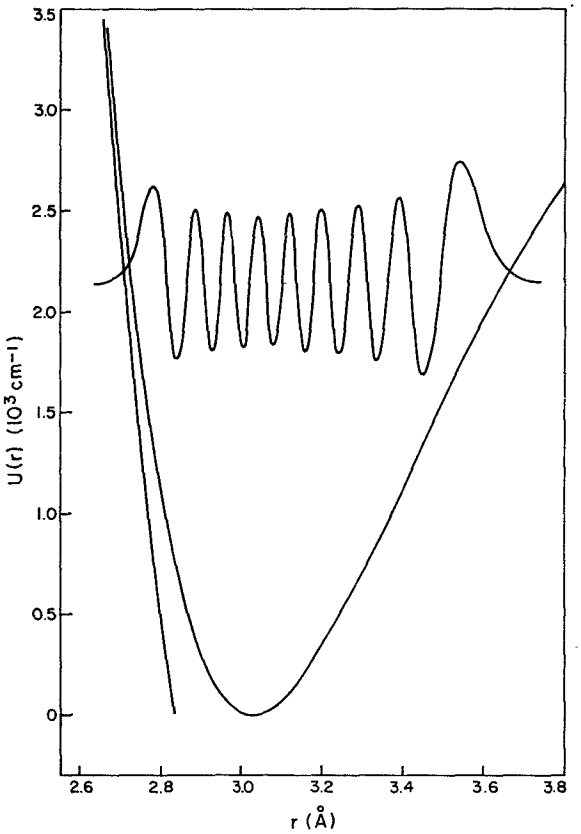

FIG. 1. Wavefunction of the level $v=16$, $J=106$ in the B state of I_2 calculated by the Rydberg–Klein–Rees procedure. The repulsive state is shown crossing the zero of energy at 2.835 Å.

Å), and levels in $v=50$, 51, 53 excited by the cadmium blue line (λ 5086 Å). All quantities on the *right* side of Eq. (3) are known or can be calculated, except $|R_e|^2$, so that one of our three pieces of information can be used to calculate a value for $|R_e|^2$, and all three will be used to determine the position of the one-parameter repulsive state causing the predissociation.

CALCULATION OF THE BOUND AND CONTINUUM WAVEFUNCTIONS

The bound-continuum vibrational overlap in Eq. (3) was evaluated by calculating the wavefunctions of the bound state $|vJ\rangle$ by the Ryberg–Klein–Rees procedure.[10] Briefly, the method here is to calculate a set of classical turning points of the B state for the rotationless ($J=0$) state from spectroscopically determined energy levels. A $J(J+1)/r^2$ barrier is then added to this potential, and the new effective potential is used to solve Schrödinger's equation for a given vibration–rotation level. The wavefunction for the level $v=16$, $J=106$ derived in this way is shown in Fig. 1.

The wavefunction of the continuum state $\langle E_c J|$ was a one-dimensional, box (energy)-normalized solution to Schrödinger's equation for a potential of the form

$$V(r)\,(\mathrm{cm}^{-1}) = (\sigma/r^{12}) + [J(J+1)/r^2] \times (\hbar N_0/4\pi c\mu) - 3209.9, \quad (4)$$

where σ is the variable position parameter, r is in Ångstrom units, and where the final constant is the energy of the $^2P_{3/2}+{}^2P_{3/2}$ atomic state relative to the zero of energy at the minimum of the B state. To carry out the integration with this potential we used the summed form of the Numerov method.[11] Here, Schrödinger's equation is written in the form $d^2\xi(r)/dr^2 = A\xi(r)$, where r is in Bohr radii (a_0) and A is $V(r)-E_c$ divided by the unit of energy $(\hbar N_0/4\pi c a_0^2\mu) = 0.948772$ cm^{-1}. The reduced solution $\xi(r)$ at each point r is related to the continuum solution $\psi(r)$ by

$$\psi(r) = \xi(r)/[1-(b^2A/12)],$$

where b is the step size.

The computation of $\psi(r)$ was carried out to a distance of 12 a_0 by which time the wavelength and peak amplitude had reached a constant value. The normalization was carried out to a large value of $r=r_\infty$ of $\sim 8\times 10^5$ a_0 and $\psi(r)$ normalized so that

$$\int_0^{r_\infty} \psi(r)^2 dr = 1.$$

The corresponding energy spacing ϵ (in cm^{-1}) of the states in the "continuum" is given by $\epsilon = 6.12013 E_c\,(\mathrm{cm}^{-1})^{1/2}/r_\infty(a_0)$ and was approximately 5×10^{-4} cm^{-1}. The final energy-normalized wavefunction was then $\langle E_c J| = \epsilon^{-1/2}\psi(r)$ which now has units of $(\mathrm{cm}^{-1})^{-1/2}$. This function is plotted in Fig. 2 for one position of the repulsive state and at the same energy E_c of the $v=16$, $J=106$ level of Fig. 1.

The step size used in the above calculations was 0.002 Å, and was slightly smaller than 0.0025 Å used in a comparable calculation by Zare.[10] This gave a sampling of about 20 points per node-to-node distance for the bound states and about 15 points for the continuum states.

COMPARISON OF CALCULATED AND OBSERVED PREDISSOCIATION RATES

In the next-to-last column of Table II we present the measured nonradiative rates at regions about $v=14$, 25, and 50. These are the differences between the total and radiative decay rates of Refs. (5)–(7) and are individually displayed in Table III of Ref. 5 for $v=14$ and 25. The radiative decay rate of levels in the region of $v=50$ was not measured (and would be extremely difficult to measure since the blending at such high v is even greater than at $v=25$), but was extrapolated from the measurements of Ref. 5. The extrapolation

[10] R. N. Zare, J. Chem. Phys. 40, 1934 (1964).

[11] M. A. Melkanoff, T. Sawada, and J. Raynal, *Methods in Computational Physics* (Academic Press Inc., New York, 1966), Vol. 6, p. 31.

takes into account the calculated linear variation of the mean cubed wavenumber of the B–X emission with v, and assumes that the electronic contribution to the transition moment in the radiation process will be constant to within about 20%.[12]

The v, J levels to which absorption takes place when I_2 is excited by atomic lines are known partly through experimental observations and can be calculated quite accurately from spectroscopic constants of the B [13] and X [14] states. Brown and Klemperer,[15] Steinfeld and Klemperer,[16] and Steinfeld *et al.*[13] have observed several transitions excited by the sodium D, mercury green, and cadmium blue lines, and the results of their observations are included in the first column of Table I. In addition to the observed lines, several more calculated lines were included in Table I which fell within 0.3 cm^{-1}

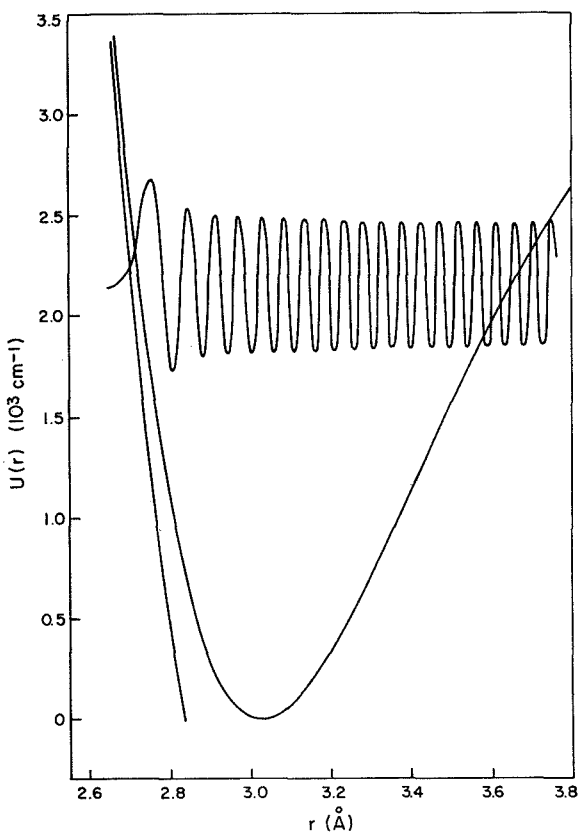

FIG. 2. Wavefunction of the continuum level at the same energy as the bound level in Fig. 1.

TABLE I. Transitions, fractional populations of the levels v, J, and weighted rotational dependences used to calculate predissociative rates from Eq. (3). The transitions in braces are those which were combined into the single J and f_{vJ} shown.

Transition		f_{vJ}	$f_{vJ}J(J+1)$
14–1 $P(107)$ 14–1 $P(114)$	$J=109$	0.288	3453
15–2 $R(43)$ 15–2 $P(38)$	$J=41$	0.563	969.5
16–2 $R(105)$		0.149	1690
25–0 $R(33)$		0.494	587.9
26–0 $R(85)$		0.432	3232
28–1 $R(50)$		0.074	196.2
50–0 $R(31)$ 50–0 $P(30)$	$J=31$	0.493	489.0
51–0 $P(45)$		0.322	637.6
53–0 $R(64)$		0.185	793.7

of the mercury green line. The additional lines 28–1 $R(50)$ and 26–0 $R(85)$ are two such lines which would get excited by a broadened green line. These transitions are also noted by Pringsheim.[17]

The fraction f_{vJ} of absorption to the level v, J was calculated for each line in the three regions by first calculating the quantity $N_{v''J''}q_{vv''}$, which is proportional to the excited-state population. Here $N_{v''J''}$ is the ground-state population of the level v'', J'' (where $J''=J\pm1$) derived from the I_2 partition function, and $q_{vv''}$ the Franck–Condon factor for the transition. The fraction f_{vJ} is the ratio of the population in the upper v, J level to the population of all levels in the region, or

$$f_{vJ}=N_{v''J\pm1}q_{vv''}/\sum_{v,J\ \text{region}} N_{v''J\pm1}q_{vv''}.$$

In order to reduce the number of overlap computations involved, several rotational transitions having neighboring J's in the same vibrational band were combined into a single transition having the square root of the average value of $J(J+1)$ and the sum of the individual f_{vJ}. These combined transitions were 14–1 $P(114)$ and $P(107)$, 15–2 $R(43)$ and $P(38)$, and 50–0 $P(30)$ and $R(31)$. The last column in Table I gives the properly weighted v, J dependence of the transition rate in Eq. (3).

RESULTS AND DISCUSSION

The position of the repulsive state of Eq. (4) was varied from 2.5 to 3.0 Å in steps of 0.05 Å. (The distances r given are those which determine, for $J=0$ in Eq. (4), the parameter σ equal to $3209.9r^{12}$.) The best fit to the experimental rates over the energy range

[12] The radiative rate was then 3.19×10^5 sec^{-1}, or approximately two times *larger* than the total rate of Ref. 6 for excitation with the Cd line. A careful remeasurement of this lifetime by P. T. Cunningham (University California Radiation Laboratory Rept. No. 18419, 1968) with better signal to noise gave a total rate of 6.58×10^5 sec^{-1}, which was used in this work.

[13] J. I. Steinfeld, J. D. Campbell, and N. A. Weiss, J. Mol. Spectry. **29**, 204 (1969); See also J. I. Steinfeld, R. N. Zare, L. Jones, M. Lesk, and W. Klemperer, J. Chem. Phys. **42**, 25 (1965).

[14] D. H. Rank and B. S. Rao, J. Mol. Spectry. **13**, 34 (1964).

[15] R. L. Brown and W. Klemperer, J. Chem. Phys. **41**, 3072 (1964).

[16] J. I. Steinfeld and W. Klemperer, J. Chem. Phys. **42**, 3475 (1965).

[17] P. Pringsheim, *Fluorescence and Phosphorescence* (Interscience Publishers, Inc., New York, 1949), p. 155.

TABLE II. Values of the vibrational overlap $\langle E_c J \mid r^{-2} \mid vJ \rangle$ for each transition studied, together with the calculated and experimental predissociation rates. The last column gives the calculated A_{nr} using the value of $\mid R_e \mid^2 = 0.00258$. The repulsive curve is at 2.835 Å (σ equal to 8.651×10^8).

Level (v, J)	$\langle E_c J \mid r^{-2} \mid vJ \rangle$ ($cm^{1/2}$ Å^{-2}) (10^{-4})	Relative rates		Absolute rates	
		Measured	Calculated	Measured (10^5 sec^{-1})	Calculated (10^5 sec^{-1})
(14,109)	4.063				
(15,41)	−5.208	1.00	1.00	2.76	2.76
(16,106)	5.154				
(25,34)	−10.70				
(26,86)	10.43	3.44	3.47	9.50	9.58
(28,51)	11.56				
(50,31)	9.271				
(51,44)	−8.966	1.23	1.15	3.39	3.18
(53,65)	−8.266				

17 300–20 000 cm^{-1} occurred at a distance of 2.835 Å, or $\sigma = 8.651 \times 10^8$. (This position is also the one drawn in Figs. 1 and 2.) The results of this fit are shown in Table II, and also in Fig. 3, where the relative rates for positions 0.002 Å to the right and left of 2.835 Å are also shown.

The results at other positions of the repulsive state can be explained qualitatively in terms of the distance between the left-hand turning points of the bound and continuum wavefunctions (see, for example, Figs. 1 and 2). As we proceed to the right (larger r) of 2.835 Å, the bound-state turning points at $v \sim 14$ and 25 approach their respective continuum-state turning points, (the overlap increases), while the bound and continuum wavefunctions at $v \sim 50$ pass through their maxima and recede. The relative predissociation rates at 2.90 Å (where the repulsive state has already crossed into the B state) then become 1.00:2.71:0.11 for the regions 14:25:50, corresponding to the passage of the continuum turning points at $v \sim 50$ away from the left-hand turning points of the B state. For distances to the left (smaller r) of 2.835 Å, the distance between the bound and continuum turning points for $v \sim 14$ and 25 is greater than at $v \sim 50$, and the relative rates are, for example, 1.00:0.31:10.9 at 2.55 Å.

We should mention at this point that although this qualitative picture is helpful, it is not quite correct to say that all the overlap occurs at the left-hand turning points. This is assumed in the delta-function approximation (i.e., a delta function in distance) to the continuum states. In our calculations at $v = 14$, 15, 16, for example, we found that the overlap at a point just after the left-hand turning point of the bound state was within a factor of 2 of its final value, indicating that considerable enhancement or cancellation occurs at the right-hand turning point. (This was to be expected for I_2 since the "wavelengths" of the bound and continuum states were within 60% of one another.) We also found that this deviation from the final value was not constant for $v \sim 14$ and 50, so that some error will occur in the *relative* values of the overlaps of these levels. Thus, we feel that numerical solutions to Schrödinger's equation will be more accurate than the delta-function approximation for cases where the kinetic energies of the overlapping states are close to one another (say, to within a factor of 10, or wavelengths within a factor of 3).

The actual values of the overlaps and the calculated and measured predissociation rates are collected in Table II. The errors in the measured rates are about ±15% of the values shown. By comparing the measured A_{nr} and the calculated overlaps in the first region ($v \sim 14$) we were able to calculate a value of the electronic overlap of the 1_u and 0^+_u states of $\mid R_e \mid^2 = 0.00258$. This value of $\mid R_e \mid^2$ was then used to calculate the absolute rates in the second and third regions.[18] (We should note that since this value of $\mid R_e \mid^2$ is a scaling factor which brings the calculated rates into agreement with the measured A_{nr}, its value is not needed for the calculation of the *relative* predissociation rates. The problem is then still the determination of the single parameter σ.)

There is some question as to whether our calculated state is the $A\ ^3\Pi_{1u}$ or $^1\Pi_{1u}$ state of I_2. Absorption to the $^3\Pi_{1u}$ state has been seen by Brown[19] and Ham,[20] and the absorption was found to have a maximum at 14 900 cm^{-1}.[20] Mulliken[21,22] has given the separation of the two states at the r_e'' of the X state (using his Interpretation I with the $^1\Pi$ at 19 470 cm^{-1}, and after taking into account the depressing effects of higher perturbing $^3\Sigma_u^+$ and $^3\Delta_{1u}$ states on the calculated $^1\Pi$–$^3\Pi$ separation) to

[18] An accurate theoretical estimate of this quantity is difficult to come by. From sum-rule considerations of transitions to *all* electronic states of the manifold, it can have at most a value of the order of unity. Van Vleck [J. Chem. Phys. **4**, 327 (1936)] has calculated for a homogeneous transition the average of the square of the electronic angular momenta about the molecular-fixed ξ and η axes for H_2, and obtains a value of 0.394. The point here is that other positions of the repulsive state in our calculations at which a good fit to the relative predissociation rates might accidentally occur give a value of $\mid R_e \mid^2$ of the order of 10^2 or greater. This comes about at distances less than 2.80 Å, where the vibrational overlap is very small, and where $\mid R_e \mid^2$ has to increase to values much greater than unity to give the experimental A_{nr}. The position of the curve at 2.835 Å thus gives a good fit to the relative rates, and provides as well a reasonable value of $\mid R_e \mid^2$.

[19] W. G. Brown, Phys. Rev. **38**, 1187 (1931).

[20] J. S. Ham, J. Am. Chem. Soc. **76**, 3886 (1954).

[21] R. S. Mulliken, Phys. Rev. **57**, 500 (1940).

[22] R. S. Mulliken (private communication).

be ~4570 cm^{-1}. At r_e'' of 2.665 Å, the energy of our calculated state is 19 300 cm^{-1}, so that the $^1\Pi$–$^3\Pi$ separation is 4400 cm^{-1}, which is close to Mulliken's prediction. The position of the $^1\Pi$ relative to the B state is estimated to be 270 cm^{-1} *above* the B state,[22] but is thought to run below the B state since no breaking-off of emission due to the predissociation has been observed. The calculated position of our repulsive state at r_e'' is 50 cm^{-1} above the B state, and quickly falls to 2000 cm^{-1} below the B state at 2.75 Å.

This last result, however, does not imply that the two states actually cross near r_e''. If the repulsive curve were at 2.832 Å, the relative rates would be 1.00:3.93:1.40, which is still within the experimental error of the observed rates in Table II. The repulsive state in this case would be 30 cm^{-1} below the B state at r_e''. We should emphasize that the potential energy of these states at $r \sim r_e''$ is changing at the rate of 40 cm^{-1}/0.001 Å, so that the 50-cm^{-1} separation is also less than the combined error in the calculation of the turning points, and more importantly, in the assumption of a one-parameter r^{-12} potential. In regard to this last point, we know that at distances less than r_e'', where the multiplet splitting is less than the singlet–triplet separation, the $^1\Pi$ must eventually lie above the $^3\Pi_{0^+u}$ state, so that an eventual crossing of the two states must occur.[21] The repulsive state of our calculation does not yet rise more rapidly than the B state at D_e', so that the exact point of crossing is difficult to estimate from our calculation, although it probably occurs above the dissociation limit of the B state.

The position of our calculated repulsive state seems to be consistent with a depressed $^1\Pi_{1u}$ lying close enough to the B state to cause some predissociation. Another piece of evidence helpful in the assignment lies in the expected[21] and observed[5] background absorption in the vicinity of the B state. Mulliken states that the $^1\Pi \leftarrow X$ absorption should be a weak one buried under the strong continuum and bands of the $B \leftarrow X$ absorption. We can get a rough estimate of the intensity of the

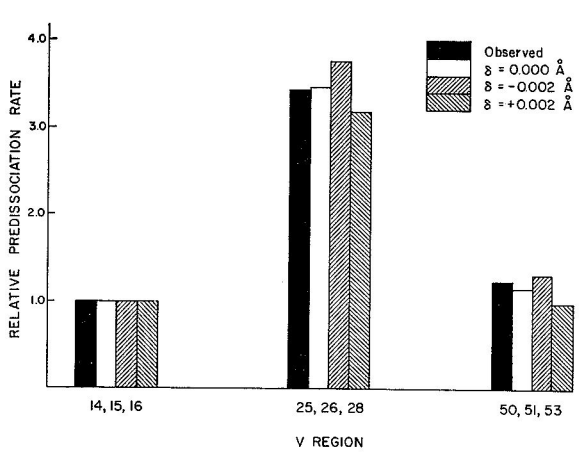

FIG. 3. Variation of the relative predissociation rates with position of the r^{-12} repulsive state. The quantity δ is the deviation from the best-fit position of 2.835 Å.

$^1\Pi \leftarrow X$ absorption from the continuum and banded absorption measurements of Ref. 5. We calculate that the average continuum absorption is 20%±10% of the banded absorption at the two wavelengths (6016 and 5460 Å) at which the continuum absorption was measured.[5] The calculation was done at each wavelength by comparing the total line strength of 50 rotational lines in a 10–12 cm^{-1} frequency interval about each wavelength with the continuum absorption over the same interval. From this continuum/banded ratio we can crudely calculate the product[21] electronic degeneracy (G') × dipole strength (D) of the $^1\Pi \leftarrow X$ to be 20%± 10% of $G'D$ for $B \leftarrow X$, or $G'D$ ($^1\Pi \leftarrow X$) = (116±58) × 10^{-4} $Å^2$. This is in rough agreement with Mulliken's estimate[22] of 67.2×10^{-4} $Å^2$, again using his Interpretation I. Although one could argue that this observed background could also be absorption into the A-state continuum, we would expect this type of absorption to be even weaker than the weak maximum A state absorption at 14 900 cm^{-1}. It seems more likely that most of the background absorption is occurring into the turning-point regions of the $^1\Pi$ state.

We can also explore the possibility of whether the A state in its known position could be causing the predissociation of the B state. A calculation of the relative predissociation rates with a Lennard-Jones 6–12 potential (with a well depth of 645 cm^{-1} and a crossing radius of 2.90 Å) gave a relative rate of 1.00:0.62:52.7 and a value of $|R_e|^2$ of 6×10^4. From these pieces of information[18] it seems almost certain that the state we have calculated is the $^1\Pi_{1u}$ state of I_2. The position and assignment of this state also explain the continuum absorption underlying the bands in the $B \leftarrow X$ system.

CONCLUSIONS

Good agreement was found between measured and calculated relative predissociation rates of three vibrational regions of the B state of I_2. The calculation assumed a repulsive r^{-12} potential for the 1_u state causing the predissociation. Both the $J(J+1)$ dependence of the heterogeneous rate as well as the relative populations of the predissociating v, J levels in each region were taken into account.

From its position relative to the A $^3\Pi_{1u}$ and B $^3\Pi_{0^+u}$ states, this calculated state is almost certainly the $^1\Pi_{1u}$ state of I_2. The presence of this state very close to the B state is consistent with the observed predissociation of the B state, and is almost certainly responsible for the observed continuum absorption underlying the B state.

ACKNOWLEDGMENTS

We are very grateful to Professor T. C. James and Professor G. A. Segal for helpful discussions and comments, and to Professor R. S. Mulliken for several helpful correspondences. Support for this work by the National Science Foundation (GP-5294) and the National Aeronautics and Space Administration (NGR-05-018-065) is also gratefully acknowledged.